

BROMINATION OF SUBSTANCES CONTAINING TWO AROMATIC NUCLEI.

Part II.—Bromination of Phenyl and Cresyl Esters of *m*- and
p-Nitro-Benzoic Acids.

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THE work described by the authors in Part I¹ has been extended to phenyl and *o*-, *m*-, *p*-cresyl esters of *m*- and *p*-nitrobenzoic acids, with a view to observe the effect of the presence of a negative group like $-NO_2$ in the acidic nucleus towards bromination. It is found that bromination proceeds readily without a carrier with phenyl *m*-nitrobenzoate and phenyl and *o*- and *m*-cresyl *p*-nitrobenzoates, while with other esters, the presence of nitric acid is necessary.

The constitution of the new mono-bromoderivatives of phenyl and *o*- and *m*-cresyl *p*-nitrobenzoates and phenyl *m*-nitrobenzoate has been confirmed by syntheses from respective bromophenols and nitroacid chlorides. The constitutions of dibromo-derivatives of *o*- and *p*-cresyl *p*-nitrobenzoates and *o*-cresyl *m*-nitrobenzoate and the tribromo derivatives of *p*-cresyl *p*-nitrobenzoate and *p*-cresyl *m*-nitrobenzoate have been assigned on the following considerations:

In view of the monobromo derivatives obtained, the possible constitutions for the dibromo derivative of *o*-cresyl *p*-nitrobenzoate are 4 : 6, 4 : 5 or 3 : 4 dibromo-*o*-cresyl *p*-nitrobenzoate. The melting point of an authentic sample of 4 : 6-dibromo-*o*-cresyl *p*-nitrobenzoate is 136-137°,² while that of the bromination product is 139-140° and the mixed melting point of these two is 115-120°. Of the remaining two possibilities the more probable is 4 : 5 because the position 3 is subject to steric hindrance. Similarly, with dibromo-*p*-cresyl *p*-nitrobenzoate the possible positions are 2 : 6, 3 : 5 or 2 : 5. The melting point of 2 : 6-dibromo-*p*-cresyl *p*-nitrobenzoate is 141-142°.³

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² Jadhav and Rangwala, *Bom. Univ. Jour.*, 1934, 3, Part II, 161-162.

³ Jadhav and Rangwala, *Bom. Univ. Jour.*, 1934, 3, Part II, 161-162.

while that of the bromination product is 165°. The constitution of the dibromo compound may therefore be 3 : 5- or 2 : 5-dibromo-*p*-cresyl *p*-nitrobenzoate.

As it has been found that the *para* directing influences of —CH₃ and —OH groups are greater than the *ortho*, and the constitution of dibromo derivative of *o*-cresyl *p*-nitrobenzoate is thought to be 4 : 5-dibromo-*o*-cresyl *p*-nitrobenzoate, the probable constitution of the dibromo-*o*-cresyl *m*-nitrobenzoate is 4 : 5-dibromo-*o*-cresyl *m*-nitrobenzoate.

The constitution of the tribromo-*p*-cresyl *p*-nitrobenzoate is 3 : 5 : 6-tribromo-*p*-cresyl *p*-nitrobenzoate as it has been obtained from the dibromo-*p*-cresyl *p*-nitrobenzoate described before and its melting point is 194-195°, while the melting point of the authentic 2 : 3 : 6-tribromo-*p*-cresyl *p*-nitrobenzoate is 159-160°.⁴ Similarly, the probable constitution for the tribromo-*p*-cresyl *m*-nitrobenzoate is also 3 : 5 : 6-tribromo-*p*-cresyl *m*-nitrobenzoate.

Experimental.

4-bromophenyl *p*-nitrobenzoate.—A mixture of phenyl *p*-nitrobenzoate (15 g.) and bromine (10 g.) was heated on a low flame for about three hours. It was then diluted with water, neutralized with sodium carbonate and the solid was finally crystallised from a mixture of alcohol and acetone in tiny white needles, m.p. 181°; yield 75%. It is soluble in acetone, chloroform, benzene and sparingly so in carbon tetrachloride and acetic acid. (Found : Br, 24.7%; C₁₃H₈O₄NBr requires Br, 24.8%).

Hydrolysis with dilute hydrochloric acid (15 c.c. acid and 10 c.c. water) in a sealed tube at 190-200° for five hours gave *p*-nitrobenzoic acid and some oil.

Mixed melting point of the bromo ester with an authentic sample of 4-bromophenyl *p*-nitrobenzoate gave no lowering.

4-bromo-*o*-cresyl *p*-nitrobenzoate.—A mixture of *o*-cresyl *p*-nitrobenzoate (4 g.) and bromine (3 g.) was heated at 140-150° for two hours. It was worked up as in the previous case and the solid crystallised from a mixture of chloroform and acetone in white shiny needles, m.p. 183-184°; yield 55%. It is soluble in acetone, chloroform, benzene, and sparingly so in carbon tetrachloride and acetic acid. (Found : Br, 23.5, C₁₄H₁₀O₄NBr requires Br, 23.8%).

Hydrolysis as in the previous case gave *p*-nitrobenzoic acid and a little black pasty mass.

Mixed melting point of the bromo ester with an authentic sample of 4-bromo-*o*-cresyl *p*-nitrobenzoate showed no lowering.

* Jadhav and Rangwala, *Bomb. Univ. Jour.*, 1934, 3, Part II, 161-162.

4-bromo-m-cresyl p-nitrobenzoate.—A mixture of *m*-cresyl *p*-nitrobenzoate (4 g.) and bromine (3 g.) was heated on a low flame for two hours, worked up as before and the solid finally crystallised from acetone in bright greyish plates, m.p. 145–146°; yield 25%. Its solubility is similar to that of the *ortho* isomer. (Found : Br, 23.7 ; $C_{14}H_{10}O_4NBr$ requires Br, 23.8%.)

It showed no lowering in melting point with a genuine sample of 4-bromo-*m*-cresyl *p*-nitrobenzoate.

4 : 5-dibromo-o-cresyl p-nitrobenzoate.—A mixture of *o*-cresyl *p*-nitrobenzoate (4 g.) and bromine (6 g.) was heated at 115–125° for two hours and worked up as usual. The solid obtained crystallised from acetone in small white needles, m.p. 139–140°; yield 25%. It resembles the monobromo derivative in solubility. (Found : Br, 38.3 ; $C_{14}H_9O_4NBr_2$ requires Br, 38.6%.)

3 : 5- or 2 : 5-dibromo p-cresyl-p-nitrobenzoate.—To a mixture of *p*-cresyl *p*-nitrobenzoate (4 g.) and bromine (6 g.), concentrated nitric acid (4 c.c.) was added and the whole heated at 110–120° for two hours and worked up as usual. The solid crystallised from acetone in white needles, m.p. 165°; yield 20%. It is soluble in acetone, chloroform, benzene and sparingly so in carbon tetrachloride and acetic acid. (Found : Br, 38.3 ; $C_{14}H_9O_4NBr_2$ requires Br, 38.6%.)

3 : 5 : 6-tribromo p-cresyl-p-nitrobenzoate.—To a mixture of 3 : 5 dibromo-*p*-cresyl *p*-nitrobenzoate (3 g.) and bromine (2 g.), concentrated nitric acid (5 c.c.) was added and the whole was heated at 150–160° for two hours. It was worked up as usual and the solid crystallised from a mixture of chloroform and acetone in woolly needles, m.p. 194–195°; yield 20%. It is soluble in chloroform and sparingly so in acetone, benzene and acetic acid. (Found : Br, 48.4 ; $C_{14}H_8O_4NBr_3$ requires Br, 48.6%.)

4-bromophenyl m-nitrobenzoate.—It was prepared in the same way as its *para* isomer and crystallised from acetone in white needles, m.p. 122°; yield 60%. It is soluble in acetone, chloroform, alcohol, benzene and acetic acid. (Found : Br, 24.7 ; $C_{14}H_8O_4NBr$ requires Br, 24.8%.)

Hydrolysis with dilute hydrochloric acid in a sealed tube at 180–200° for five hours gave *m*-nitrobenzoic acid and some oil.

The bromo ester showed no lowering in melting point with a genuine sample of 4-bromophenyl *m*-nitrobenzoate.

4 : 5-dibromo-o-cresyl m-nitrobenzoate.—To a mixture of *o*-cresyl *m*-nitrobenzoate (4 g.) and bromine (6 g.) fuming nitric acid (8 c.c.) was added and the whole heated on a waterbath for eight hours. The mixture was worked up as before and the solid crystallised from a mixture of chloroform

and acetone in white needles, m.p. 170°; yield 30%. It is soluble in acetone, chloroform, benzene and sparingly so in carbon tetrachloride and acetic acid. (Found: Br, 38.4; $C_{14}H_9O_4NBr_2$ requires Br, 38.6%.)

3 : 5 : 6-tribromo-*p*-cresyl *m*-nitrobenzoate.—To a mixture of *p*-cresyl *m*-nitrobenzoate (4 g.) and bromine (9 g.), fuming nitric acid (10 c.c.) was added and the whole heated on a waterbath for eight hours. It was worked up as usual and the solid crystallised from acetone in woolly needles, m.p. 193–194°; yield 20%. It is soluble in acetone, chloroform, benzene, carbon tetrachloride and sparingly so in acetic acid. (Found: Br, 48.4; $C_{14}H_8O_4NBr_3$ requires Br, 48.6%.)

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